BENJAMIN J. CAYETANO
GOVERNOR OF HAWAII

BRUCE S. ANDERSON, Ph.D., M.P.H.
DIRECTOR OF HEALTH

STATE OF HAWAII
DEPARTMENT OF HEALTH
P. O. BOX 3378
HONOLULU, HAWAII 96801

In reply, please refer to:
HEER OFFICE

POLICY UPDATE

Technical Guidance Manual for the Implementation of The Hawaii State Contingency Plan

TO ALL INTERESTED PARTIES:

This policy update establishes the Hawaii Department of Health, Office of Hazard Evaluation and Emergency Response (HEER) requirement for the use of U.S. Environmental Protection Agency (EPA) SW-846 Method 5035 "Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples" as modified by the HEER Office. Effective January 1, 2002, all new Sampling and Analysis Plans (SAPs) must specify that volatile organic compound analysis by EPA Methods 8015B, 8021B, and 8260B for the HEER Office shall be collected in accordance with EPA Method 5035. Effective March 1, 2002, all volatile organic compound analysis shall be conducted on samples collected using EPA Method 5035. EPA Method 5035 attempts to minimize loss of volatile organic compounds and offers a variety of options for collection of soil and other solid matrix samples. The need for and use of each sample collection option shall be based on site-specific requirements and data quality objectives.

Please bring this policy update to the attention of anyone you know who may have an interest in this matter. Should you have any questions regarding this policy update, please contact the Office of Hazard Evaluation and Emergency Response at (808) 586-4249.

KEITH KAWAOKA, Manager
Office of Hazard Evaluation and
Emergency Response

IMPLEMENTATION OF METHOD 5035

"Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples"

Background

Currently, the Hawaii Department of Health (DOH) policy allows soil and other solid matrix samples for volatile organic compound (VOC) analysis to be collected and analyzed following the procedures in U.S. Environmental Protection Agency (EPA) Method 5030. The samples are packed in Teflon-lined screw-cap containers, kept cool during transport to the laboratory, and analyzed within 14 days of collection. Research over the years has shown that this process has led to significant losses of VOCs, some quite dramatic. Evaluation of improved methods for preserving VOCs in soil led EPA to the development and adoption of Method 5035.

In June 1997, EPA promulgated *Update III of Test methods for Evaluating Solid Waste (SW-846)*. As part of this update, Method 5030A "Sample Preparation of Volatile Organic Compounds for Purge-and-Trap Analysis" for soil and other solid matrix samples was deleted, and Method 5035 "Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples" was added.

EPA Method 5035 identifies procedures to collect and prepare soil and solid matrix samples for VOC analysis using Methods 8015B, 8021B, and 8260B. This method describes a closed-system purge and trap process for the analysis of low concentration VOCs in solid materials (e.g. soils, sediments, and solid waste). This method is also designed for use on samples containing high concentrations of VOCs and for oily waste, which are purged using Method 5030.

This method was established to minimize the biodegradation of volatile organic compounds through the use of preservatives that eliminated the organisms of biodegradation or through freezing of the sample to immobilize their activity. The holding times were also re-evaluated to allow for maximum recovery of volatile organic constituents. Method 5035 minimizes or eliminates exposure of the soil core to the atmosphere preventing further losses of VOCs. This DOH policy update is an interpretation on the implementation of EPA SW-846 Method 5035 for all remediation projects subject to investigation and cleanup under Chapter 128D, HRS.

DOH Policy on the Implementation of Method 5035

A review of Method 5035 indicates that several options exist for anyone planning on conducting a sampling event for VOCs. The DOH has selected specific

options in order to keep VOC losses to a minimum. DOH prefers that all samples be collected in 40 mL VOAs with PTFE-faced silicone septa and preserved with sodium bisulfate in the field. DOH understands that site-specific circumstances may require other options and has provided for these situations (see Table 1).

Samples anticipated to contain VOC concentrations at less than 200 µg/kg may be preserved by freezing or with the use of a preservative (sodium bisulfate) prior to analysis, either in the field at the time of collection or at the laboratory within 48 hours of collection. The sodium bisulfate preservative must be added to the soil and other solid matrix samples anticipated to contain VOCs at concentrations less than 200 µg/kg. Enough sodium bisulfate should be present to ensure a sample pH of less than 2. If the samples will be preserved at the laboratory, the samples must be collected in a Purge-and-Trap Sampler ™, an Encore ™ sampler, a 40-mL VOA fitted with PTFE septum, or other equivalent sampling device (with DOH approval) and delivered to the laboratory for preservation within 48 hours of sample collection. Addition of the preservative in the lab must be done with a minimum exposure of the soil core to air.

A methanol preservative must be added to soil and other solid matrix samples anticipated to contain VOCs at concentrations greater than 200 µg/kg (Table 2). The first option is to collect a bulk sample in a VOA vial or suitable container without the preservative solution. A portion of the sample is removed from the container in the laboratory within 48 hours of collection and is dispersed in a water-miscible solvent (e.g. methanol) to dissolve the volatile organic constituents. Surrogates are added to the vial, then an aliquot of the solvent is removed from the vial, and purged using Method 5030 and analyzed by an appropriate determinative method.

For soil samples that are composed of an aggregate of particle sizes that prevents sampling with a syringe or Encore ™ sampler, it may be necessary to collect a bulk sample in a wide mouth sample jar with sufficient preservative as specified in Method 5035, sodium bisulfate for sample concentrations less than 200 ug/Kg or methanol for sample concentrations of 200 ug/Kg or more. A portion of the bulk sample will be removed in the laboratory for analysis within 48 hours of sample collection.

Readers should refer to EPA SW-846, Update III, Method 5035 for specific procedures on the sample collection and preservation options appropriate for their site. The use of each option must be based on site-specific requirements and data quality objectives. Because there are options for low concentration (VOCs < 200 µg/kg) and high concentration (VOCs > 200 µg/kg), the selected option must reflect the requirements outlined in DOH's Risk-Based Corrective Action (that is, Tier I Action Levels) or other investigation or closure standards applicable to a particular site. It is recommended that multiple sample aliquots be collected to allow for screening, analysis and reanalysis.

Preservation:

- **Freezing of unpreserved samples**

At this time, the DOH HEER Office will allow freezing of unpreserved samples to increase the sample holding time to 7 days prior to analysis. It has been shown that freezing is an effective means of slowing the biodegradation process. Samples should be frozen in containers that have an airtight seal that will remain airtight while frozen. Freezing of samples will allow unpreserved samples to be stored for more than 48 hours prior to analysis, thus accommodating shipping time to a U.S. Mainland laboratory.

- **Preservative**

For low concentration sample preservation, Method 5035 calls for the use of approximately 1 gram of sodium bisulfate and 5 mL of organic-free reagent water in each sample container. Sodium bisulfate, NaHSO4 of ACS reagent grade or equivalent is recommended. To each vial, a soil core (plug) of 5 grams will be added. It is estimated that approximately 0.2 g of sodium bisulfate will be used to preserve each 1 g of sample, which should be enough to ensure a sample pH of $\leq$ 2.

For high concentration sample preservation, methanol will preserve and extract VOCs from the soil core. Methanol of purge-and-trap quality or equivalent should be used.

- **Calcareous Soils**

For calcareous soils that effervesce on contact with the sodium bisulfate preservative solution, the DOH HEER Office recommends that effervescing samples be collected in a device such as an Encore ™ sampler, stored at or below 0 degrees Celsius. Alternatively, soil cores collected in Encore ™ samplers must be transfer to an appropriate sample holder and this transfer should be done while the sample is frozen.

Sampling Containers:

- DOH HEER Office highly recommends the use of VOA vial with PTFE lined silicon septa.

- An Encore ™ sampler may also be used if stored at 4^{o}C $\pm$ 2^{o}C and analyzed within 48 hours or when preserved by freezing or by the

addition of the preservative within 48 hours of collection or analyzed within 7 days if frozen in the field.

- A wide-mouth jar may also be required to collect bulk samples in circumstances in which a core sample cannot be easily obtained.

- An Purge-and-Trap Sampler ^{TM} may also be used if stored at 4^{o}C $\pm$ 2^{o}C and analyzed within 48 hours or when preserved by freezing or by the addition of the preservative within 48 hours of collection or analyzed within 7 days if frozen in the field.

Soil Moisture Determination:

- DOH HEER Office highly recommends collecting soil samples for soil moisture determination and report the result on a dry weight basis.

U.S. EPA Region 9 Interim Policy for Determination of VOC Concentrations in Soil and Solid Matrices

Many State and Federal environmental programs have incorporated EPA Method 5035 into their regulations or programs. The U.S. EPA Region 9 office released a regional interim policy dated June 23, 1999 outlining the requirements for sampling and laboratory methodologies to minimize the loss of VOCs from soil and other solid matrices. The U.S. EPA Region 9 policy requires the use of EPA Method 5035 or an equally or more effective method for sampling and analyzing VOCs in soil and other solid matrices. This EPA policy is applicable to federal facilities, entities complying with EPA regulatory requirements and other entities producing data for EPA decision-making, and EPA grantees. The U.S. EPA Region 9 policy is attached as Appendix A.

Implementation Period

EPA Method 5035 represents a significant departure from former EPA Method 5030A; therefore, the DOH HEER Office will allow a transition period for implementing EPA Method 5035. After January1, 2002, only soil and solid matrix samples collected and analyzed using the options outlined in EPA Method 5035 and this policy update will be acceptable by the DOH HEER Office for volatile organic compound analyses.

TABLE 1: Method 5035 – Low Concentration Samples (≤ 200 ug/Kg)

Sample Device	**Sample container**	**Preservative**	**Field Temp.**	**Shipping Temp.**	**Holding Time (field +shipping)**	**Notes**	**Lab Temp.**	**Lab**	**Total Holding time**
EnCore	EnCore	None	$4^oC \pm 2^oC$	$4^oC \pm 2^oC$	48 hours	48 hours at 4^oC	$4^oC \pm 2^oC$	Lab w/ equipment	48 hours
EnCore	EnCore	None	Frozen	Frozen	48 hours	48 hours at 4^oC	$4^oC \pm 2^oC$	Lab w/ equipment	48 hours + shipping
EnCore	EnCore	None	Frozen	Frozen	7 days		Frozen	Lab w/ equipment	7 days
EnCore	EnCore	None	$4^oC \pm 2^oC$	$4^oC \pm 2^oC$	48 hours	48 hours at 4^oC	$4^oC \pm 2^oC$	Lab w/ equipment	48 hours
EnCore	EnCore	$NaHSO_4$ added in the lab	$4^oC \pm 2^oC$	$4^oC \pm 2^oC$	14 days		$4^oC \pm 2^oC$	Lab w/ equipment	14 days
Syringe	40 mL VOA (stir rod & water)	None	$4^oC \pm 2^oC$	$4^oC \pm 2^oC$	48 hours	48 hours at 4^oC	$4^oC \pm 2^oC$	Lab w/ autosampler	48 hours
Syringe	40 mL VOA (stir rod & water)	None	Frozen	Frozen	48 hours	48 hours at 4^oC	$4^oC \pm 2^oC$	Lab w/ autosampler	48 hours + shipping time
Syringe	40 mL VOA (stir rod & water)	None	Frozen	Frozen	7 days		Frozen	Lab w/ autosampler	7 days
Syringe	40 mL VOA (stir rod & water)	$NaHSO_4$	$4^oC \pm 2^oC$	$4^oC \pm 2^oC$	14 days		$4^oC \pm 2^oC$	Lab w/ autosampler	14 days
Syringe	40 mL VOA (water)	None	$4^oC \pm 2^oC$		2 hours	2 hours at 4^oC		Onsite GC	2 hours

Laboratories must be equipped with the appropriate autosampler or En Novative product.

Holding time for unfrozen or unpreserved samples is 48 hours when stored at $4^oC \pm 2^oC$. Analysis or preservation must be performed immediately.

TABLE 2: Method 5035 – High Concentration Samples (>200ug/Kg)

Sample Device	Sample container	Preservative	Field Temp.	Shipping Temp.	Holding Time (field +shipping)	Notes	Lab Temp.	Lab	Total Holding time
Syringe	Jar for bulk sample	None	$4^{o}C \pm 2^{o}C$	$4^{o}C \pm 2^{o}C$	48 hours	48 hours at $4^{o}C$	$4^{o}C \pm 2^{o}C$	Lab w/ autosampler	48 hours
Syringe	40 mL VOA	Methanol	$4^{o}C \pm 2^{o}C$	$4^{o}C \pm 2^{o}C$	30 days	At $4\ ^{o}C$	$4^{o}C \pm 2^{o}C$	Lab w/ autosampler	30 days
Syringe	40 mL VOA	None	$4^{o}C \pm 2^{o}C$		2 hours	2 hours at $4^{o}C$		Onsite GC	2 hours

Laboratories must be equipped with the appropriate autosampler.

Holding time for unpreserved samples is 48 hours when stored at $4^{o}C \pm 2^{o}C$. Analysis or preservation must be performed immediately.